

# THERMODYNAMIC PROPERTIES AND CRYSTALLIZATION KINETICS AT HIGH LIQUID UNDERCOOLING

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## Abstract

The heat capacities of liquid and crystalline Au-Pb-Sb alloys in the glass-forming composition range were measured with droplet emulsion and bulk samples. Based on the measured  $C_p$  data, the entropy, enthalpy, and Gibbs free energy functions of the eutectic, solid mixture and undercooled liquid were determined as a function of undercooling and compared with theoretical predictions. The results indicate an isentropic temperature at  $313 \pm 5$  K, which agrees well with experimental data for the glass transition. A kinetics analysis of the nucleation undercooling response suggests that the proper choice for the Gibbs free energy change during crystallization is most important in analyzing the nucleation kinetics. By classical nucleation theory, the prefactors obtained, based on a variety of theoretical predictions for the driving force, can differ by six orders of magnitude. If the nucleation rates are extrapolated to high undercooling, the extrapolations based on measured heat capacity data show agreement, whereas the predicted nucleation rates are inconsistent with results from drop tower experiments. The implications for  $\mu\text{g}$  experiments are discussed.

## Introduction

In order to predict the crystalline or amorphous transformation products during solidification from an undercooled liquid, knowledge of the thermodynamic properties of the metastable liquid is necessary. In particular, the entropy and enthalpy differences between the crystalline and undercooled liquid phases are of interest and can be evaluated from available heat capacity data. Experimentally, deep undercooling levels of a liquid can be attained by slow cooling of a droplet emulsion [1]. Droplet samples were prepared by shearing a mixture of carrier fluid and liquid alloy (99.99% purity) under an inert atmosphere into an emulsion ( $\sim 10^7$  droplets) with an average diameter of  $10\ \mu\text{m}$ , thus effectively isolating potential nucleation sites. Applying a relatively noncatalytic coating, crystallization can be prevented in a temperature range up to  $0.3$  to  $0.4\ T_m$  on a time scale long enough to allow measurements of thermophysical properties of the undercooled liquid. The emulsification approach allows glass formation in droplet samples during slow cooling ( $10$ – $20$  K/min) in a few alloy systems [1]. This method has been applied to Au-Pb-Sb alloys [2] with compositions close to the ternary eutectic and within the experimentally determined glass formation range [3].

The undercooling, heat capacity  $C_p$ , and reaction kinetics were measured with a well-calibrated differential scanning calorimeter, Perkin-Elmer DSC7, under computer control. For  $C_p$  measurements, three different scans are compared: (1) an empty pan of equivalent mass, (2) sapphire as standard for calibration, and (3) the sample itself. Bulk samples are used for  $C_p$  measurements of the stable liquid and crystalline phases. The  $C_p$  measurements of the undercooled liquid are based on a differential measurement of  $C_p$  by comparing one sample containing carrier fluid, liquid, and a small amount of X of solid with a second sample containing carrier fluid and the liquid completely crystallized [2]. From the knowledge of X ( $\sim 10\%$ ), the specific heat of the crystalline phase  $C_p^X$  and the measured heat capacity difference  $\Delta C_p$ ,  $C_p$  of the undercooled liquid is obtained (within  $\pm 5\%$ ) as  $C_p^L = [\Delta C_p + (1 - X)C_p^X]/(1 - X)$ .

For evaluation of the nucleation kinetics during crystallization from the highly undercooled liquid, the cooling rate has been varied between 0.16 and 5 K/s and is related to the measured nucleation temperatures taken at the onset of the nucleation exotherm. With the nucleation temperatures corrected for instrumental temperature lag, the reaction kinetics are analyzed in terms of classical nucleation theory. During continuous cooling at low rates, the onset of solidification occurring within the time  $t$  in a droplet of catalytic surface area  $a$ , the following relation holds [4]:

$$\ln t = -\ln A + B/\Delta G_v^2 T \quad (1)$$

with the prefactor term  $A = a\Omega_a/[K\eta(T)]$  and the interfacial energy related term  $B = b\sigma_{xL}^3 f(\theta)/k_B$ . Here,  $\Omega_a$  is the prefactor of the nucleation frequency;  $K$  is a constant on the order of 100; the liquid shear viscosity  $\eta$  is given by  $\eta(T) = 10^{-3.3} \exp[3.34 T_E/(T - T_{go})]$  with  $T_{go}$  being the ideal glass transition temperature [5];  $b = 16\pi/3$  is a geometrical factor;  $\sigma_{xL} f(\theta)$  is the crystal/liquid interfacial energy; and  $\Delta G_v$  is the free energy difference per unit volume between the undercooled liquid and crystalline phase. The dependence of the cooling rate  $\dot{T}$  on the undercooling level  $\Delta T$  (temperature difference between the eutectic temperature  $T_E$  and nucleation temperature  $T_N$ ) is measured by DSC with the time  $t$  corresponding to  $\Delta T/\dot{T}$ . This allows us to determine the operating nucleation kinetics in terms of  $A$  and  $B$  from the experimental data.

## Results and Discussion

Using droplet samples, a maximum undercooling level of  $\sim 0.3 T_L$  (175 K) below the liquidus temperature  $T_L$  was achieved at a cooling rate of 0.33 K/s, resulting in a single, well-defined crystallization exotherm [2]. The composition closest to the ternary eutectic composition and still in the glass-forming range [3] was found as  $\text{Au}_{53.2}\text{Pb}_{27.5}\text{Sb}_{19.3}$  with the eutectic temperature  $T_E$  at 523 K and  $T_L$  at 573 K. The heat of fusion  $\Delta H_f$  of this alloy is  $\Delta H_f = 8.25 \text{ kJmole}^{-1}$  with a corresponding entropy of fusion  $\Delta S_f = 15.78 \text{ JK}^{-1}\text{mole}^{-1}$ .

The measured heat capacities of bulk and droplet samples are fitted numerically by the following equations:  $C_p^L = -47.4 + 9.4 \cdot 10^{-2} T + 1.11 \cdot 10^7 T^{-2} \text{ JK}^{-1}\text{mole}^{-1}$  and  $C_p^x = 29.1 + 5.9 \cdot 10^{-3} T \text{ JK}^{-1}\text{mole}^{-1}$ , and are shown in Fig. 1. The heat capacity of the undercooled liquid exhibits a continuous rise of  $C_p$  with decreasing temperature. This effect is much more pronounced for glass-forming alloys like Au-Pb-Sb than for pure metals [6] and has important consequences for the thermodynamic properties of the undercooled liquid and evaluation of the crystallization kinetics.

From the  $C_p$  data, the thermodynamic properties of the undercooled liquid  $L$  and eutectic solid  $X$  can be derived below the eutectic temperature  $T_E$ . For the current purpose, the differences in entropy  $\Delta S$  (integration over  $\Delta C_p^L/T \text{ dT}$ ), enthalpy  $\Delta H$  (integration over  $\Delta C_p^L \text{ dT}$ ), and free energy  $\Delta G (= \Delta H - T\Delta S)$  between undercooled liquid and crystalline solid are determined. The entropy difference is considered as one of the main parameters describing the ability of an alloy to form a glass, and is shown in Fig. 2. The entropy of the undercooled liquid decreases faster than the entropy of the stable crystalline phase when the temperature is reduced. If the entropy values are extrapolated beyond the experimentally determined range (indicated by the dashed line in Fig. 2) an isentropic temperature  $T_{\Delta S=0}$  is found at  $313 \pm 5 \text{ K}$  (within the error range of the  $C_p$  measurement). Below this temperature the entropy of the undercooled liquid would become smaller than that of the crystal. This situation can be avoided

by massive freezing of the liquid in a glass (Kauzmann paradox [7]). Thus, the isentropic temperature  $T_{\Delta S=0}$  indicates the ultimate undercooling limit of a liquid in order to prevent an "entropy crisis," and corresponds to the ideal glass transition temperature  $T_{go}$ . The estimated temperature  $T_{go}$  agrees well with the experimentally observed glass transition temperature by heating an Au-Pb-Sb glass through  $T_g$  [2]. It corresponds to  $0.6 T_E$  (the reduced-glass transition temperature) in comparison to  $0.25 T_m$  for pure metals [8], thus characterizing the easy glass-forming ability of Au-Pb-Sb alloys.

The enthalpy difference  $\Delta H$  is also included in Fig. 2. It is found that solidification under adiabatic conditions [9] becomes possible below  $T_h = 365$  K. This temperature marks the start of the hypercooled regime, where the enthalpy of the undercooled liquid equals the enthalpy of the eutectic solid at the eutectic temperature and is only about 35 K below the average nucleation temperature in the droplet population at a cooling rate of 0.33 K/s.

In addition to the determination of the thermodynamic properties in the metastable regime, the droplet samples have also been used for determination of the crystallization kinetics. For these samples, the nucleation temperature decreased from 425.2 K to 419.9 K if the cooling rate was varied from 0.16 K/s to 5 K/s. The kinetics measurements are analyzed by plotting the measured response time  $t$  ( $= \Delta T/\dot{T}$ ) versus  $(\Delta G_V^2 T)^{-1}$  based on the experimentally determined heat capacity data. From classical nucleation theory, Eq. (1), A and B are then given as  $A = 1.8 \cdot 10^{16} \text{ sec}^{-1}$  and  $B = 1.02 \cdot 10^8 \text{ KJ}^{-2} \text{ cm}^{-6}$ .

An important parameter in the analysis of the kinetics of crystallization at high undercooling is the Gibbs free energy difference between metastable liquid and crystalline solid  $\Delta G_V$  and its dependence on temperature. Because  $C_p$  is unknown in most cases, different models have been proposed for  $\Delta G_V$  using such easily accessible data as the heat of fusion  $\Delta H_f$ , the heat capacity difference  $\Delta C_p^f$  at the eutectic temperature  $T_E$ , and the undercooling level  $\Delta T = T_E - T$  below the eutectic temperature. Several approaches for crystallization of a single solid phase are given below, such as

$$\Delta G_V = \Delta H_f \Delta T / T_E \quad (2a) \quad [10]$$

$$\Delta G_V = \Delta H_f \Delta T / T_E - [\Delta C_p^f (\Delta T)^2 (1 - \Delta T / 6T)] / 2T \quad (2b) \quad [11]$$

$$\Delta G_V = \Delta H_f \Delta T \cdot 2T / [T_E (T_E + T)] \quad (2c) \quad [12]$$

$$\Delta G_V = \Delta H_f \Delta T \cdot T / (T_E)^2 \quad (2d) \quad [13]$$

Figure 3 represents different approximations proposed for  $\Delta G_V$  including the experimentally derived values. It is seen that at low undercooling, all formulae predict basically the same  $\Delta G_V$  in excellent agreement with the experimental curve. At modest undercooling, the best correlation between experimental data and the proposed models over the measured temperature range is obtained with Eq. (2b) [11] and Eq. (2c) [12]. As has been found earlier, Turnbull's approximation, Eq. (2a), gives an upper limit for  $\Delta G_V$  and is close to values obtained for pure metals [6], whereas Hoffman's expression underestimates  $\Delta G_V$  in the case of glass-forming metallic alloys. In addition, the Kauzmann temperatures  $T_{\Delta S=0}$ , where  $-\partial \Delta G_V / \partial T$  equals 0, are indicated in Fig. 3 and summarized in Table I. They are all lower than the Kauzmann temperature extrapolated from the measured  $C_p$  data and differ considerably for the different models ranging from  $-\infty$  Eq. (2a) [10] to 261 K Eq. (2d) [13].

One consequence of the correct evaluation of  $\Delta G_V$  relates to the proper interpretation of crystallization kinetics [4]. The measured prefactor term A is in good agreement with the classical nucleation theory for heterogeneous nucleation ( $\Omega_a = \sim 10^{23} \text{ cm}^{-3} \text{ sec}^{-1}$  [5]) if only a small portion ( $10^{-3}$ ) of the surface area presents an active catalytic site for crystallization. Using the same type of analysis as outlined above for the experimentally derived nucleation data and

basing  $\Delta G_V$  on Eqs. (2a) to (2d) would lead to a large difference in the prefactor term A in the nucleation rate expression as given in Table I. Whereas  $\Delta G_V$  differs only about 20% at 420 K for the different models, the derived constants A can vary by six orders of magnitude ranging from  $A = 2.4 \cdot 10^{13} \text{ sec}^{-1}$ , Eq. (2a), to  $1.1 \cdot 10^{19} \text{ sec}^{-1}$ , Eq. (2d), in comparison to  $1.8 \cdot 10^{16} \text{ sec}^{-1}$  for the experimentally derived value. Furthermore, the slope B shows only a small dependence on the model with a variation of less than 10%.

Based upon the factors A and B given in Table I, it is possible to develop the transformation diagrams that are described by Eq. (1). Especially for glass-forming alloys, the temperature dependence of the prefactor term A, i.e., the viscosity change of the undercooled liquid as a function of undercooling, should be taken into account. This can be done by appropriately correcting the factor A, which was determined in a narrow range of the nucleation temperatures  $T_N$  as  $A(T) = A(T_N)\eta(T_N)/\eta(T)$ . Then the steady-state transformation diagrams are calculated using the modified prefactors A(T), and the corresponding extrapolated Kauzmann temperatures  $T_{\Delta S = 0}$  taken as critical temperature for the viscosity  $T_{go}$ .

**Table I:** Analysis of nucleation kinetics according to classical nucleation theory Eq. (1) and different models for the Gibbs free energy difference  $\Delta G_V$ . The Kauzmann temperature  $T_{\Delta S = 0}$  is given for the different  $\Delta G_V$  models.

$\Delta G_V \text{ (J/cm}^3\text{)}$	$T_{\Delta S = 0} \text{ (K)}$	$A \text{ (sec}^{-1}\text{)}$	$B \text{ (K J}^{-2} \text{ cm}^{-6}\text{)}$
experimental	313	$1.8 \cdot 10^{16}$	$1.02 \cdot 10^8$
(2a) Ref. 10	$-\infty$	$2.4 \cdot 10^{13}$	$1.03 \cdot 10^8$
(2b) Ref. 11	209	$2.1 \cdot 10^{15}$	$0.99 \cdot 10^8$
(2c) Ref. 12	216	$1.2 \cdot 10^{16}$	$0.97 \cdot 10^8$
(2d) Ref. 13	261	$1.1 \cdot 10^{19}$	$0.93 \cdot 10^8$

Whereas a linear approximation for  $\Delta G_V$  is not applicable for glass-forming alloys ( $T_{go} = -\infty$ ), all other approximations [11–13] depict the "nose" of the transformation curve at considerably shorter times (between  $3 \cdot 10^{-4}$ /s [13] and  $5 \cdot 10^{-6}$ /s [11]). According to this analysis, much higher cooling rates would be required for curves (b), (c), and (d), in order to avoid crystallization than the experimentally determined critical cooling rate of  $\sim 10^3 \text{ K/s}$  using drop tube processing [2]. The only curve that is consistent with the experimental observation that crystallization is avoided at cooling rates of  $\sim 10^3 \text{ K/s}$  is represented by the curve (exp) that is based on the measured  $C_p$  data. Consequently, the  $\Delta G_V$  models as given by Eqs. (2a) to (2d) are inappropriate for analysis of the crystallization kinetics of glass-forming Au-Pb-Sb alloys at high undercooling.

Moreover, the effects of non-steady-state nucleation have been considered [14]. Such transient effects are becoming important at temperatures below 400 K for this alloy system with the "noses" in Fig. 3 only slightly shifted to shorter times. These effects are negligible above 400 K and, therefore, do not affect the critical cooling rate required for glass formation in Au-Pb-Sb. Nevertheless, due to the Stokes–Einstein relation commonly used for non-steady-state nucleation analysis, the viscosity and transient nucleation effects are strongly coupled. Because diffusivity data are unknown in the highly undercooled state, it is very difficult to separate the two effects at high undercooling. Because of the lack of an appropriate theory for the glass transition itself and the lack of knowledge of many important dynamical properties of highly undercooled liquids including the viscosity  $\eta$ , diffusion coefficients D, and transient times  $\tau$ , the correct description of the crystallization kinetics or glass formation in the highly undercooled regime cannot be simply reduced to existing models for the free energy difference  $\Delta G_V$ . It is shown here that the best extrapolation possible is when experimental data for the

nucleation rates are available based on crystallization kinetics and thermodynamic data for the free energy functions measured at low and modest undercooling.

### Implications for Microgravity

The described emulsification method is applicable for metals and alloys with low melting points and gives insight into the fundamentals of crystallization and glass formation. Due to the lack of appropriate carrier fluids, this method is not generally applicable to metals or alloys with high melting points that are of more substantial technological interest. Therefore, we propose to use containerless processing methods, such as levitation melting under UHV conditions, preferably in a  $\mu\text{g}$  environment, to study the thermophysical properties of the undercooled liquid state of alloys with high  $T_m$  over sufficiently long time scales. It turns out in the above analysis that the most important parameter for a correct description of crystallization kinetics and glass formation is the heat capacity of the undercooled liquid which allows estimates of  $\Delta G_v$  and  $T_{go}$  (the ideal glass transition temperature and critical temperature for the viscosity in the Vogel-Fulcher equation). A method has been proposed to measure  $C_p$  of the undercooled liquid state under  $\mu\text{g}$  by an a.c. pulse method described in detail elsewhere [15]. Together with the knowledge of additional thermophysical properties including the viscosity and diffusion coefficients, the above analysis can then be applied to a broader class of materials. Glass-forming alloys exhibit a more pronounced temperature dependence of  $C_p$  and  $\eta$  than pure metals and, therefore, appear to present the best candidates for thermophysical property measurements of the undercooled liquid state under  $\mu\text{g}$  conditions.

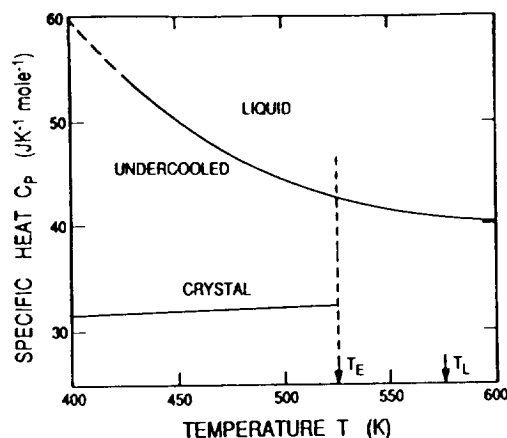
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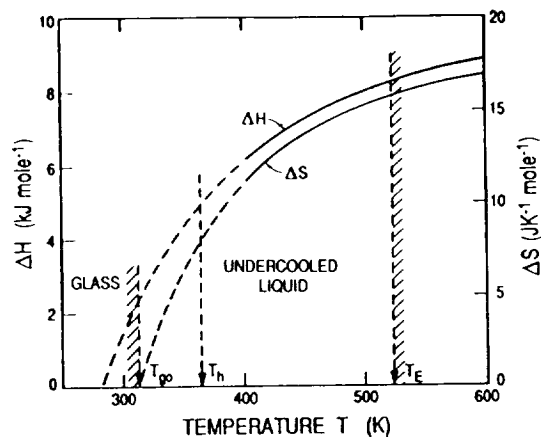
### REFERENCES

- [1] J. H. Perepezko and J. S. Smith, *J. Non-Cryst. Solids* **44** (1981): 65.
- [2] M. C. Lee, H. J. Fecht, J. L. Allen, J. H. Perepezko, K. Ohsaka, and W. L. Johnson, *J. Mat. Sci. Eng.* **97** (1988): 301.
- [3] C. O. Kim and W. L. Johnson, *Phys. Rev. B* **23** (1981): 143.
- [4] J. H. Perepezko, B. A. Mueller, and K. Ohsaka, *Hume-Rothery Memorial Symposium on Undercooled Alloy Phases*, edited by E. W. Collings and C. C. Koch, The Metallurgical Society, New Orleans, LA (1986): 289.
- [5] C. V. Thompson and F. Spaepen, *Acta Metall.* **31** (1983): 2021.
- [6] J. H. Perepezko and J. S. Paik, *J. Non-Cryst. Solids* **61&62** (1984): 113.
- [7] W. Kauzmann, *Chem. Rev.* **43** (1948): 219.
- [8] H. J. Fecht and W. L. Johnson, *Nature* **334** (1988): 50.
- [9] J. H. Perepezko and Rasmussen, *Met. Trans. A* **9** (1978): 1490.
- [10] D. Turnbull and J. C. Fisher, *J. Chem. Phys.* **17** (1949): 71.
- [11] K. S. Dubey and P. Ramachandrarao, *Acta Metall.* **32** (1984): 91.
- [12] C. V. Thompson and F. Spaepen, *Acta Metall.* **27** (1979): 1855.
- [13] J. D. Hoffman, *J. Chem. Phys.* **29** (1958): 1192.

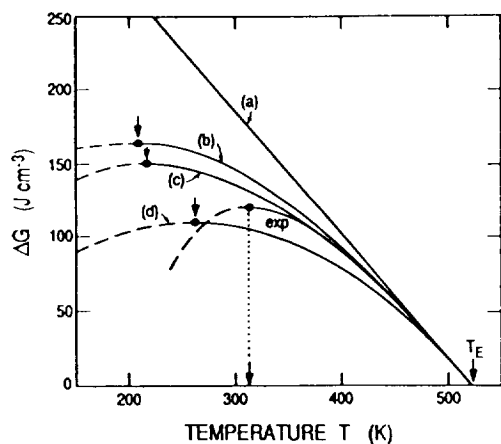
- [14] K. F. Kelton and A. L. Greer, *J. Non-Cryst. Solids* **79** (1986): 295.
- [15] H. J. Fecht and W. L. Johnson, "A Conceptual Approach for Non-Contact Calorimetry in Space," *Rev. Sci. Instr.* (1990).



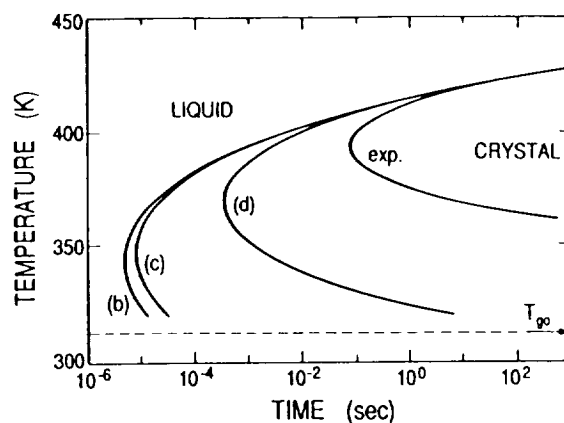
**Fig. 1:** Heat capacity data measured for liquid and crystalline Au<sub>53.2</sub>Pb<sub>27.5</sub>Sb<sub>19.3</sub> alloys.



**Fig. 2:** The entropy and enthalpy differences  $\Delta S$  and  $\Delta H$  between undercooled liquid and crystalline eutectic solid based on measured (solid line) and extrapolated (dashed line)  $C_p$  data. The isotropic temperature  $T_{go}$  is obtained as  $313 \pm 5$  K, close to the experimental glass transition temperature. The hypercooling regime starts below the isenthalpic temperature  $T_h = 365$  K.



**Fig. 3:** Free energy difference between  $\Delta G_V$  of the undercooled liquid and eutectic solid per unit volume based on different approximations including the experimental data. Curves (a) to (d) refer to Eqs. (3a) to (3d) respectively. The ideal glass transition temperature is indicated by the zero slope for  $\Delta G_V$ .



**Fig. 4:** Calculated steady-state heterogeneous nucleation kinetics of glass-forming Au-Pb-Sb alloys based on Eq. (1) for experimental  $C_p$  data (exp), and approximations for  $\Delta G_V$  and  $T_{\Delta S=0}$  according to Eqs. (3b) to (3d). Consistency with drop tower experiments (glass formation at  $\sim 10^3$  K/s) is only found for the curve (exp).